JC07 Rec'd PCT/PTO 11 MAR 2002

FORM PTO-1390 (Modified) (REV 11-98) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

# TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER
**JMYT-258US**

U.S. APPLICATION NO (IF KNOWN, SEE 37 CFR 1.5)
**Not Yet Assigned** 10/070873

| INTERNATIONAL APPLICATION NO. | INTERNATIONAL FILING DATE | PRIORITY DATE CLAIMED |
|---|---|---|
| **PCT/GB00/03379** | **04 September 2000 (04.09.00)** | **10 September 1999 (10.09.99)** |

TITLE OF INVENTION
**REGENERATING SULFUR POISONED DIESEL CATALYSTS**

APPLICANT(S) FOR DO/EO/US
**TWIGG, Martyn Vincent**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
   - b ☐ has been transmitted by the International Bureau.
   - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   - a ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   - b. ☐ have been transmitted by the International Bureau.
   - c ☐ have not been made; however, the time limit for making such amendments has NOT expired
   - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). (UNEXECUTED)
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409)
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U S C 371 (c)(5))

**Items 13 to 20 below concern document(s) or information included:**

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1 98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3 28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☒ Certificate of Mailing by Express Mail
20. ☐ Other items or information:

10/070873 JC10 Rec'd PCT/PTO 11 MAR 2002

| U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) | INTERNATIONAL APPLICATION NO. | ATTORNEY'S DOCKET NUMBER |
|---|---|---|
| Not Yet Assigned | PCT/GB00/03379 | JMYT-258US |

| 21. The following fees are submitted:. | | | | CALCULATIONS | PTO USE ONLY |
|---|---|---|---|---|---|
| **BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5)) :** | | | | | |
| ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO . . . . . . . . . . **$970.00** | | | | | |
| ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but Internation Search Report prepared by the EPO or JPO . . . . . . **$840.00** | | | | | |
| ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . . . . . . . **$690.00** | | | | | |
| ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . . . . . . . . **$670.00** | | | | | |
| ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . . . . . . . **$96.00** | | | | | |
| **ENTER APPROPRIATE BASIC FEE AMOUNT =** | | | | **$890.00** | |
| Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)). | | | | **$0.00** | |
| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE | | |
| Total claims | 12 - 20 = | 0 | x $18.00 | **$0.00** | |
| Independent claims | 2 - 3 = | 0 | x $84.00 | **$0.00** | |
| Multiple Dependent Claims **(check if applicable).** | | | ☐ | **$0.00** | |
| **TOTAL OF ABOVE CALCULATIONS =** | | | | **$890.00** | |
| Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) **(check if applicable)** ☐ | | | | **$0.00** | |
| **SUBTOTAL =** | | | | **$890.00** | |
| Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). + | | | | **$0.00** | |
| **TOTAL NATIONAL FEE =** | | | | **$890.00** | |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).** ☐ | | | | **$0.00** | |
| **TOTAL FEES ENCLOSED =** | | | | **$890.00** | |
| | | | | **Amount to be: refunded** | $ |
| | | | | **charged** | $ |

☒ A check in the amount of **$890.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No in the amount of to cover the above fees A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **18-0350** A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:


**Christopher R. Lewis**
**RATNER & PRESTIA**
**Suite 301 One Westlakes, Berwyn**
**P.O. Box 980**
**Valley Forge, PA 19482-0980**

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SIGNATURE

**Christopher R. Lewis**
NAME

**36,201**
REGISTRATION NUMBER

**March 11, 2002**
DATE

JMYT-258US

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | | |
|---|---|---|
| Applicant: | Martyn Vincent Twigg | : Art Unit: |
| Application No.: | To Be Assigned | : Examiner: |
| Filed: | Herewith | : |
| FOR: REGENERATING SULFUR POISONED DIESEL CATALYSTS | | : |

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, DC 20231

SIR:

Prior to examination, please amend the above-identified application as follows.

IN THE SPECIFICATION:

Please replace the paragraph beginning at page 2, line 10 with the following:

According to one aspect, the invention provides a diesel (compression ignition) engine (which typically operate at approximately $\lambda = 3$, with a range of between 1.5 (high load) and 5 (low load/idle)) having combustion management means and an exhaust gas aftertreatment system without a $NO_x$ trap, which system comprising a platinum group metal (PGM) catalyst liable to be poisoned by fuel sulfur to cause significant degradation of catalyst performance, which engine is fuelled, at least intermittently, by a diesel fuel containing such levels of sulfur as to cause poisoning of the catalyst, wherein the combustion management means is effective to modulate the air/fuel ratio ($\lambda$) to 0.90, preferably 0.95, or richer to provide a series of peak enrichments for a time which is in aggregate sufficient to cause release of significant quantities of sulfur-containing species from the catalyst or catalyst components, and wherein each regeneration is for 10 seconds to 10 minutes, whereby the catalyst is regenerated.

Please replace the paragraph beginning at page 3, line 5 with the following:

Modern diesel engine designs are tending towards so-called "common-rail" fuel injection systems. The use of these are particularly preferred in the present invention because of the ability to control quantity and timing of fuel injection. Accordingly, one method of operating the present invention is to incorporate, during the enriched operating conditions, such a quantity of fuel post combustion in the main power stroke, as to reach in the exhaust gases, $\lambda$ of 0.95 or richer. This may be achieved by generally known means. The post combustion enrichment may be in one or more of the cylinders, providing that the overall air/fuel ratio reaches 0.95 or richer. Of course, the quantity of air may be restricted as an alternative, or in addition, providing that driveability is not noticeably affected.

Please replace the paragraph beginning at page 6, line 4 with the following:

The catalyst in its stainless steel enclosure was then removed from the car and fitted to the exhaust system of a four-cylinder engine capable of operating slightly rich. It was coupled to a dynamometer mounted on a bench. The fuel used contained 250 ppm sulfur. The catalyst was exposed to exhaust gas corresponding to $\lambda = 0.95$ for a total period of 5 minutes at a maximum of 500°C. The average temperature was 450°C. After this treatment the catalyst was refitted to the car and retested in the standard way, with the following results: 0.119 and 0.257 g/km for hydrocarbon and carbon monoxide respectively.

<u>IN THE CLAIMS</u>:

Please cancel claim 10 and replace claims 1-7, 9, and 11 with the following amended claims:

1. (Amended) A diesel (compression ignition) engine having combustion management means and an exhaust gas aftertreatment system without a $NO_x$ trap, which system comprising a platinum group metal (PGM) catalyst liable to be poisoned by fuel sulfur to cause significant degradation of catalyst performance, which engine is fuelled, at least intermittently, by a fuel containing such levels of sulfur as to

cause poisoning of the catalyst, wherein the combustion management means is effective to modulate the air/fuel ratio (λ) in pulses to 0.90 or richer to provide a series of peak enrichments of from 250 milliseconds to 5 seconds in duration for an aggregate time of from 10 seconds to 10 minutes, whereby the catalyst is regenerated.

2. (Amended) An engine according to claim 1, wherein the combustion management means is effective to modulate the air/fuel ratio pulses to 0.95 or richer.

3. (Amended) An engine according to claim 1, wherein the catalyst is an oxidation catalyst.

4. (Amended) An engine according to claim 1, incorporating "common rail" fuel injection, programmed to provide in at least one cylinder, such a quantity of fuel post combustion in the main power stroke, so as to reach, in the exhaust gases, λ of 0.90 or richer.

5. (Amended) An engine according to claim 1, wherein the catalyst is an oxidation catalyst and the exhaust gas aftertreatment system also includes a particle or soot filter downstream of the catalyst.

6. (Amended) An engine according to claim 1, wherein it is fuelled with diesel fuel containing at least 250 ppm sulfur.

7. (Amended) A method of regenerating a PGM catalyst poisoned by sulfur in the exhaust gas aftertreatment system of an internal combustion engine, which system does not include a $NO_x$ trap, which method comprising modulating the air/fuel ratio (λ) of the exhaust gases passing through the catalyst to 0.90 or richer to provide a series of peak enrichments of from 250 milliseconds to 5 seconds in duration for an aggregate time of from 10 seconds to 10 minutes, whereby the catalyst is regenerated.

9. (Amended) Method according to claim 7, wherein the catalyst is in the temperature range 200-500°C, preferably 350-500°C, during regeneration.

Claim 10 has been canceled.

11. (Amended) Method according to claim 7, wherein the exhaust gas is derived from diesel fuel containing at least 250ppm sulfur.

Please add the following new claim:

12. (Newly Added) A method according to claim 7, wherein $\lambda$ in the exhaust gases is 0.95 or richer.

Respectfully submitted,

Christopher R. Lewis, Reg. No. 36,201
Attorney for Applicants

CRL/lrb
Enclosure: Version with Markings to Show Changes Made

Dated: March 11, 2002

Suite 301
One Westlakes, Berwyn
P.O. Box 980
Valley Forge, PA 19482-0980
(610) 407-0700

The Assistant Commissioner for Patents is hereby authorized to charge payment to Deposit Account No. **18-0350** of any fees associated with this communication.

**EXPRESS MAIL** Mailing Label No.: EV 029154255 US
Date of Deposit: March 11, 2002

I hereby certify that this paper and fee are being deposited, under 37 C.F.R. § 1.10, and with sufficient postage, using the "Express Mail Post Office to Addressee" service of the United States Postal Service on the date indicated above and that the deposit is addressed to the Assistant Commissioner for Patents, Washington, DC 20231.

Kathleen Libby

VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE SPECIFICATION:

At page 2, line 10:

According to one aspect, the invention provides a diesel (compression ignition) engine (which typically operate at approximately $\lambda = 3$, with a range of between 1.5 (high load) and 5 (low load/idle)) having combustion management means and an exhaust gas aftertreatment system without a $NO_x$ trap, which system comprising a platinum group metal (PGM) catalyst liable to be poisoned by fuel sulfur to cause significant degradation of catalyst performance, which engine is fuelled, at least intermittently, by a diesel fuel containing such levels of sulfur as to cause poisoning of the catalyst, wherein the combustion management means is effective to modulate the air/fuel ratio ($\lambda$) to 0.90, preferably 0.95, or richer to provide a series of peak enrichments for a time which is in aggregate sufficient to cause release of significant quantities of sulfur-containing species from the catalyst or catalyst components, and wherein each regeneration is for 10 seconds to 10 minutes, whereby the catalyst is regenerated.

At page 3, line 5:

Modern diesel engine designs are tending towards so-called "common-rail" fuel injection systems. The use of these are particularly preferred in the present invention because of the ability to control quantity and timing of fuel injection. Accordingly, one method of operating the present invention is to incorporate, during the enriched operating conditions, such a quantity of fuel post combustion in the main power stroke, as to reach in the exhaust gases, ~~8~~ $\lambda$ of 0.95 or richer. This may be achieved by generally known means. The post combustion enrichment may be in one or more of the cylinders, providing that the overall air/fuel ratio reaches 0.95 or richer. Of course, the quantity of air may be restricted as an alternative, or in addition, providing that driveability is not noticeably affected.

At page 6, line 4:

The catalyst in its stainless steel enclosure was then removed from the car and fitted to the exhaust system of a four-cylinder engine capable of operating slightly rich. It was coupled to a dynamometer mounted on a bench. The fuel used contained 250 ppm sulfur. The catalyst was exposed to exhaust gas corresponding to ~~8~~ $\lambda = 0.95$ for a total period of 5 minutes at a maximum of 500°C. The average temperature was 450°C. After this treatment the catalyst was refitted to the car and retested in the standard way, with the following results: 0.119 and 0.257 g/km for hydrocarbon and carbon monoxide respectively.

IN THE CLAIMS:

1. (Amended) A diesel (compression ignition) engine having combustion management means and an exhaust gas aftertreatment system without a $NO_x$ trap, which system comprising a platinum group metal (PGM) catalyst liable to be poisoned by fuel sulfur to cause significant degradation of catalyst performance, which engine is fuelled, at least intermittently, by a fuel containing such levels of sulfur as to cause poisoning of the catalyst, wherein the combustion management means is effective to modulate the air/fuel ratio ($\lambda$) in pulses to 0.90~~, preferably 0.95,~~ or richer to provide a series of peak enrichments of from 250 milliseconds to 5 seconds in duration for ~~a~~ an aggregate time ~~which is in aggregate sufficient to cause release of significant quantities of sulfur-containing species from the catalyst or catalyst components, and wherein each regeneration is for~~ of from 10 seconds to 10 minutes, whereby the catalyst is regenerated.

2. (Amended) An engine according to claim 1, wherein the combustion management means is effective to ~~cause pulses of~~ modulate the air/fuel ratio ~~modulation of from 250 milliseconds to 5 seconds in duration within each regeneration event~~ pulses to 0.95 or richer.

3. (Amended) An engine according to claim 1 ~~or 2~~, wherein the catalyst is an oxidation catalyst.

4. (Amended) An engine according to claim 1, incorporating "common rail" fuel injection, programmed to provide in at least one cylinder,

such a quantity of fuel post combustion in the main power stroke, so as to reach, in the exhaust gases, ~~a~~ $\lambda$ of 0.90 or richer.

5. (Amended) An engine according to claim 1, ~~2, 3 or 4,~~ wherein the catalyst is an oxidation catalyst and the exhaust gas aftertreatment system also includes a particle or soot filter downstream of the catalyst.

6. (Amended) An engine according to ~~any preceding~~ claim 1, wherein it is fuelled with diesel fuel containing at least 250ppm sulfur.

7. (Amended) A method of regenerating a PGM catalyst poisoned by sulfur in the exhaust gas aftertreatment system of an internal combustion engine, which system does not include a $NO_x$ trap, which method comprising modulating the air/fuel ratio ($\lambda$) of the exhaust gases passing through the catalyst~~, to $\lambda$ = 0.90, preferably 0.95,~~ in pulses to 0.90 or richer to provide a series of peak enrichments of from 250 milliseconds to 5 seconds in duration for ~~a~~ an aggregate time ~~which is in aggregate sufficient to cause release of significant quantities of sulfur-containing species from the catalyst or catalyst components, and wherein each regeneration is for~~ of from 10 seconds to 10 minutes, whereby the catalyst is regenerated.

9. (Amended) Method according to claim 7 ~~or 8~~, wherein the catalyst is in the temperature range 200-500°C, preferably 350-500°C, during regeneration.

Claim 10 has been canceled.

11. (Amended) Method according to claim 7~~, 8, 9 or 10~~, wherein the exhaust gas is derived from diesel fuel containing at least 250ppm sulfur.

Claim 12 has been added.

13 Rec'd PCT/PTO 12 AUG 2002

JMYT-258US

PATENT

10/070873

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | | |
|---|---|---|
| Applicant: | Martyn Vincent Twigg | : Art Unit: |
| Application No.: | 10/070,873 | : Examiner: |
| Filed: | Herewith | : |
| FOR: REGENERATING SULFUR POISONED DIESEL CATALYSTS | | : |

**SUPPLEMENTAL PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents
Washington, DC 20231

SIR:

Prior to examination, please amend the above-identified application as follows.

IN THE SPECIFICATION:

Please add the following paragraph at page 1, after the title:

This application is the U.S. national phase application of PCT International Application No. PCT/GB00/03379.

Respectfully submitted,

Christopher R. Lewis, Reg. No. 36,201
Attorney for Applicants

CRL/lrb
Enclosure: Version with Markings to Show Changes Made

Dated: August 12, 2002

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(610) 407-0700

The Assistant Commissioner for Patents is hereby authorized to charge payment to Deposit Account No. **18-0350** of any fees associated with this communication.

**EXPRESS MAIL** Mailing Label No.: EV 108523598 US
Date of Deposit: August 12, 2002

I hereby certify that this paper and fee are being deposited, under 37 C.F.R. § 1.10, and with sufficient postage, using the "Express Mail Post Office to Addressee" service of the United States Postal Service on the date indicated above and that the deposit is addressed to the Assistant Commissioner for Patents, Washington, DC 20231.

Kathleen Libby

VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE SPECIFICATION:

IN THE SPECIFICATION:

At page 1, after the title:

This application is the U.S. national phase application of PCT International Application No. PCT/GB00/03379.

13 Rec'd PCT/PTO 11 MAR 2002
10/070873
ART 34 AMDT



# REGENERATING SULFUR POISONED DIESEL CATALYSTS

This invention concerns improving diesel catalyst performance, especially where the catalyst is a catalyst in the exhaust gas from a diesel engine fuelled by "higher sulfur" fuel.

It is well known that fuels, including gasoline or diesel (gas-oil) fuels containing relatively high sulfur content, e.g. about 350 ppm in the case of diesel fuel, lead to a number of disadvantages when trying to clean-up the exhaust gases by some form of catalytic aftertreatment. During the combustion process, sulfur in the fuel is converted to sulfur dioxide ($SO_2$) which poisons in particular platinum catalysts. The platinum catalyst itself catalyses the oxidation of $SO_2$ to $SO_3$ which adsorbs strongly onto the surfaces of platinum particles and is extremely effective as a catalyst poison. Further contributions to poisoning problems arise from the formation of base metal sulfates from the other components of a catalyst formulation, which sulfates can act as a reservoir for poisoning sulfur species within the catalyst.

A number of catalysts may be used in association with such lean combustion engines as diesel engines, including oxidation catalysts, $NO_x$ storage catalysts and the combination of platinum oxidation catalyst and a particle filter/trap which utilises the formation of $NO_2$ from NO in the exhaust gases, and the combustion of trapped sooty particles by reaction with the $NO_2$. This system is described in, for example, our EP-A-0341832 and such systems are commercially available as the "CRT"™. In all these cases, the unavailability of low (<50ppm) sulfur fuel, even for one or two tankfuls, can seriously degrade the performance of the catalyst, and performance may never recover fully, or some other damage may be caused to the engine system or catalyst system.

There is therefore a real need for a system or a method of operation that will permit either the occasional tank filling with high sulfur fuel or even more continuous operation using high sulfur fuel, without causing undue damage to the catalyst or the complete system.

We have previously proposed, in WO99/11910, a system for the reduction of sulfur poisoning in an underfloor catalyst, by the initiation of an engine operating system, e.g. by

AMENDED SHEET

enriching the exhaust gases with CO and/or hydrocarbon, to raise the temperature of the catalyst to at least 550°C. Such a system has particular application to a gasoline-fuelled engine operating as a stoichiometric ($\lambda = 1$) engine.

We have now discovered that by performing a series of regeneration events a "little-and-often", catalytic activity of sulfur poisoned diesel catalysts can be recovered to a greater extent than when regeneration is performed following extended periods of sulfation.

According to one aspect, the invention provides a diesel (compression ignition) engine having combustion management means and an exhaust gas aftertreatment system without a $NO_x$ trap, which system comprising a platinum group metal (PGM) catalyst liable to be poisoned by fuel sulfur to cause significant degradation of catalyst performance, which engine is fuelled, at least intermittently, by a diesel fuel containing such levels of sulfur as to cause poisoning of the catalyst, wherein the combustion management means is effective to modulate the air/fuel ratio ($\lambda$) to 0.90, preferably 0.95, or richer to provide a series of peak enrichments for a time which is in aggregate sufficient to cause release of significant quantities of sulfur-containing species from the catalyst or catalyst components, and wherein each regeneration is for 10 seconds to 10 minutes, whereby the catalyst is regenerated.

The combustion management means may initiate the necessary level of enrichment according to a pre-determined frequency, or in response to a condition indicating catalyst poisoning or the danger of catalyst poisoning, for example by some form of sensing of sulfur levels either directly or indirectly. This may be achieved, for example by on-board diagnostics indicating that the catalyst is no longer performing in the correct and appropriate manner.

The combustion management means ideally forms part of a conventional electronic engine control unit.

Conventional Diesel engines normally operate under lean conditions, with a considerable excess of oxygen over that required for combustion of the hydrocarbon fuel.

However, some engines may operate at a slightly rich condition in some parts of their load/speed map. Such regions can be extended by appropriate control of fuelling, EGR rates, and if necessary throttling air intake to one or more of the cylinders.

Modern diesel engine designs are tending towards so-called "common-rail" fuel injection systems. The use of these are particularly preferred in the present invention because of the ability to control quantity and timing of fuel injection. Accordingly, one method of operating the present invention is to incorporate, during the enriched operating conditions, such a quantity of fuel post combustion in the main power stroke, as to reach in the exhaust gases, 8 of 0.95 or richer. This may be achieved by generally known means. The post combustion enrichment may be in one or more of the cylinders, providing that the overall air/fuel ratio reaches 0.95 or richer. Of course, the quantity of air may be restricted as an alternative, or in addition, providing that driveability is not noticeably affected.

It is envisaged that the simplest method of operating is to cause enrichment to a pre-determined level for the necessary time. However, it may be more advantageous to ramp up to either a peak or a plateau, or to carry out a series of peak enrichments. The ideal format may be determined for any particular engine and catalyst system by routine testing. The enrichment profile may be varied according to operating conditions.

We believe, although we do not wish to be restricted by theory, that the present invention permits the release of sulfur both as $SO_2$ and as $SO_3$ from a poisoned catalyst surface. It is preferred to avoid catalyst components which store or retain sulfur species.

The air/fuel ratio necessary for successful regeneration depends on the temperature, and the catalyst concerned. For practically convenient temperatures to be effective normally $\lambda = 1$, or a slightly leaner environment is required, suitably to $\lambda = 1.1$. Regeneration times are lower with more strongly reducing conditions. Typically $\lambda = 0.95$ is appropriate at temperatures in the range 250-500°C. More strongly reducing conditions can result in formation of increasing amounts of undesirable hydrogen sulphide ($H_2S$). This has a disagreeable odour, and is itself a powerful catalyst poison that strongly adsorbs to metal catalyst surfaces. Accordingly, present indications are that $\lambda = 0.90$ to 1.1 is a suitable range.

According to a further aspect, the invention provides A method of regenerating a PGM catalyst poisoned by sulfur in the exhaust gas aftertreatment system of a diesel engine, which system does not include a $NO_x$ trap, which method comprising modulating the air/fuel ration ($\lambda$) of the exhaust gases passing through the catalyst, to $\lambda = 0.90$, preferably 0.95, or richer to provide a series of peak enrichments for a time which is in aggregate sufficient to cause release of significant quantities of sulfur-containing species from the catalyst or catalyst components, and wherein each regeneration is for 10 seconds to 10 minutes, whereby the catalyst is regenerated.

Desirably, during the enriched operating condition, catalyst temperatures are in the range 200-500°C, preferably 350-500°C, although other temperatures may be used, up to 600°C or more.

In general, increasing the catalyst temperature decreases the time necessary to achieve maximum regeneration, and increasing time at temperature increases the degree of reactivation. Accordingly, our initial tests have been successful with regeneration times of from 10 seconds to 5 minutes. A suitable time is therefore considered to be from 2 seconds to 10 minutes, preferably in the form of shorter times or pulses, for example 250 milliseconds to 5 seconds.

In a particularly preferred embodiment, the exhaust gas aftertreatment system includes an oxidation catalyst and a downstream particulate or soot filter i.e. it includes our CRT™ system as described in EP-A-0341832. According to this aspect, the invention provides an engine according to the invention wherein the catalyst is an oxidation catalyst and the exhaust gas aftertreatment system also includes a particle or soot filter downstream of the catalyst.

Gas flow rate has an effect on the time necessary to complete regeneration, and suitable space velocities for the exhaust gases are in the range 5,000 to 50,000 $hour^{-1}$.

Although post combustion injection into the engine cylinder is, at present, the preferred method of operation according to the present invention, the invention

encompasses direct injection into the exhaust gases, which may be in or close to the exhaust manifold, or into or close upstream of the catalyst housing.

The following Examples illustrate prior art methods and arrangements and provide useful background for understanding the present invention.

## EXAMPLE 1

A standard production 1997 model year European passenger car with a five cylinder 2.5 litre displacement direct injection Diesel engine that was calibrated to meet European Stage 2 emission levels was used without modification to the engine or its management systems.

The car's exhaust system was equipped with a single round platinum-based oxidation catalyst located in an underfloor position. The catalyst comprised a cordierite monolith having 400 cells/inch$^2$ (62 cells cm$^{-2}$), with an external diameter of 5.66 inch (14.38 cm) and length 6 inch (15.24 cm), carrying a washcoat with a platinum loading of 90g/ft$^3$ (3.18 g l$^{-1}$).

The vehicle was tested according to the Stage 3 European procedure, without any idle period. In each case the results given are the average of three independent measurements, and are expressed as grams of pollutant/km, which were derived in the normal way. In all of the tests the $NO_x$ figures were similar, but the $NO_2/NO$ ratio depended on the catalyst activity. In this experiment only hydrocarbon and carbon monoxide tail pipe measurements were made.

The exhaust gas directly from the engine contained 0.340 and 1.074 g/km hydrocarbon and carbon monoxide respectively.

With the fresh catalyst the tailpipe hydrocarbon and carbon monoxide figures were 0.102 and 0.195 g/km respectively. However, after 17600 km road operation with diesel fuel typically containing 350 ppm sulfur the tailpipe emissions had risen to 0.287 and 0.823 g/km for hydrocarbons and carbon monoxide respectively. Changing the fuel to a grade containing 38 ppm sulfur followed by normal driving for 1500 km did not

significantly improve the catalyst performance. The tail-pipe emissions were 0.247 and 0.808 g/km for hydrocarbon and carbon monoxide respectively.

The catalyst in its stainless steel enclosure was then removed from the car and fitted to the exhaust system of a four-cylinder engine capable of operating slightly rich. It was coupled to a dynamometer mounted on a bench. The fuel used contained 250 ppm sulfur. The catalyst was exposed to exhaust gas corresponding to 8 = 0.95 for a total period of 5 minutes at a maximum of 500°C. The average temperature was 450°C. After this treatment the catalyst was refitted to the car and retested in the standard way, with the following results: 0.119 and 0.257 g/km for hydrocarbon and carbon monoxide respectively.

These experiments show the oxidation performance of a catalyst deactivated through use with sulfur containing fuel can be reactivated by a short reductive process, even in the presence of sulfur.

## EXAMPLE 2

A similar platinum-based catalyst to that in Example 1, that had been road aged (with fuel containing typically 350 ppm sulfur) for 18240 km on the same car as in Example 1, gave the following tail pipe emissions in a European Stage 3 test: 0.270 and 0.856 g/km for hydrocarbon and carbon monoxide respectively.

A core (25 mm diameter, 38 mm long) from the middle of this catalyst was taken with the aid of a diamond tipped tool. The sample was placed into a laboratory test unit. A gas flow containing 400 ppm carbon monoxide, 300 ppm nitric oxide, 100 ppm propene, 12% oxygen, 4.5% water, 4.5% carbon dioxide, and 20 ppm sulfur dioxide with nitrogen balance was established through the catalyst core at a rate corresponding to a space velocity of 60 x $10^3$ $hour^{-1}$. The conversion of nitric oxide to nitrogen dioxide over the catalyst was 19% at 300°C.

The catalyst core was then subjected to a reductive regeneration procedure at $\lambda$ = 0.95, with the same space velocity as before. The $\lambda$ = 0.95 condition was obtained by

increasing the proportion of carbon monoxide and propene, and decreasing the flow of oxygen. The temperature was gradually increased to 450°C over 15 minutes, during which time a large amount of sulfur dioxide was liberated from the catalyst that was detected by a mass spectrometer. No hydrogen sulphide was detected by the mass spectrometer, nor was any carbonyl sulphide. It was determined that 0.56 wt% of sulfur absorbed on the catalyst had been liberated. These tests showed that the catalyst activity recovered as sulfur was removed.

The gas composition was then reset to that used initially, and the nitric oxide conversion to nitrogen dioxide measure to be 63% at 300°C, showing the ability of the regeneration procedure to reactivate catalyst for the oxidation of nitric oxide to nitrogen dioxide.

**CLAIMS:**

1. A diesel (compression ignition) engine having combustion management means and an exhaust gas aftertreatment system without a $NO_x$ trap, which system comprising a platinum group metal (PGM) catalyst liable to be poisoned by fuel sulfur to cause significant degradation of catalyst performance, which engine is fuelled, at least intermittently, by a diesel fuel containing such levels of sulfur as to cause poisoning of the catalyst, wherein the combustion management means is effective to modulate the air/fuel ratio ($\lambda$) to 0.90, preferably 0.95, or richer to provide a series of peak enrichments for a time which is in aggregate sufficient to cause release of significant quantities of sulfur-containing species from the catalyst or catalyst components, and wherein each regeneration is for 10 seconds to 10 minutes, whereby the catalyst is regenerated.

2. An engine according to claim 1, wherein the combustion management means is effective to cause pulses of air/fuel ratio modulation of from 250 milliseconds to 5 seconds in duration within each regeneration event.

3. An engine according to claim 1 or 2, wherein the catalyst is an oxidation catalyst.

4. An engine according to claim 3, incorporating "common rail" fuel injection, programmed to provide in at least one cylinder, such a quantity of fuel post combustion in the main power stroke, so as to reach, in the exhaust gases, □ of 0.90 or richer.

5. An engine according to claim 1, 2, 3 or 4, wherein the catalyst is an oxidation catalyst and the exhaust gas aftertreatment system also includes a particle or soot filter downstream of the catalyst.

6. An engine according to any preceding claim, wherein it is fuelled with diesel fuel containing at least 250ppm sulfur.

7. A method of regenerating a PGM catalyst poisoned by sulfur in the exhaust gas aftertreatment system of a diesel engine, which system does not include a $NO_x$ trap,

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which method comprising modulating the air/fuel ration (λ) of the exhaust gases passing through the catalyst, to $\lambda = 0.90$, preferably 0.95, or richer to provide a series of peak enrichments for a time which is in aggregate sufficient to cause release of significant quantities of sulfur-containing species from the catalyst or catalyst components, and wherein each regeneration is for 10 seconds to 10 minutes, whereby the catalyst is regenerated.

8. Method according to claim 7, wherein λ in the exhaust gases is in the range 0.95 to 1.1 during regeneration.

9. Method according to claim 7 or 8, wherein the catalyst is in the temperature range 200-500°C, preferably 350-500°C, during regeneration.

10. Method according to claim 7, 8, or 9, wherein regeneration is carried out using pulses of air/fuel ratio modulation of from 250 milliseconds to 5 seconds in duration.

11. Method according to claim 7, 8, 9 or 10, wherein the exhaust gas is derived from diesel fuel containing at least 250ppm sulfur.

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**(54) Title:** REGENERATING SULPHUR POISONED DIESEL CATALYSTS


**(57) Abstract:** A diesel (compression ignition) engine having combustion management means and an exhaust gas aftertreatment system without an $NO_x$ trap, which system comprising a platinum group metal (PGM) catalyst liable to be poisoned by fuel sulphur to cause significant degradation of catalyst performance, which engine is fuelled, at least intermittently, by a diesel fuel containing such levels of sulphur as to cause poisoning of the catalyst, wherein the combustion management means is effective to modulate the air/fuel ratio (λ) to 0.90, preferably 0.95, or richer for a time which is in aggregate sufficient to cause release of significant quantities of sulphur-containing species from the catalyst or catalyst components, whereby the catalyst is regenerated.

# Declaration and Power of Attorney For Patent Application
## English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled
REGENERATING SULFUR POISONED DIESEL CATALYSTS,
the specification of which is attached hereto unless the following box is checked:

☒ was filed on March 11, 2002 as
United States Application Number or PCT International Application Number 10/070,873
and was amended on March 11, 2002.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

| Prior Foreign Application(s) | | | Priority Not Claimed |
|---|---|---|---|
| 9921376.1 | Great Britain | 10 September 1999 | |
| (Number) | (Country) | (Day/Month/Year Filed) | ☐ |
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| (Application Number) | (Filing Date) |
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| (Application Number) | (Filing Date) |

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

PCT/GB00/03379 ✓ | September 4, 2000 ✓ | Abandoned
(Application Number) | (Filing Date) | (Status - patented, pending, abandoned)

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POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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☐ Additional Inventors are being named on separately numbered sheets attached hereto.